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Raman Effect and Molecular Structure.

By

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Abstract.

On the view that a great majority of the Raman lines are caused by transitions corresponding to fundamental vibration frequencies of the molecules involved in the scattering process, an interpretation of the Raman spectra of various simple molecules is attempted on the basis of dynamical considerations. Following Dennison, suitable assumptions regarding the form of the energy functions have been made and the characteristic oscillations of models like X_2, X_3, X_4 and AX_2, AX_3 and AX_4 have been investigated. The theoretical results are correlated with those recently obtained by the author from a study of the Raman spectra in a number of simple molecules to which one or other of the above structures can be assigned.

All diatomic oscillators have one vibrational frequency, examples being those of H_2, N_2, O_2 and Cl_2. A system like X_3 arranged at the corners of an equilateral triangle, represented by ozone which however is not studied in this paper, has two fundamental frequencies. The model of X_4 has 4 and 3 frequencies respectively according as it is a square or a tetrahedron. The molecule of phosphorus is found to have three Raman frequencies and hence presumably a tetrahedral structure. The third of these is very prominent in the scattering and corresponds to a radial expansion of the tetrahedron.

AX_2 has 3 and 2 frequencies respectively according as it is a bent or a linear model. The cases of SO_2 representing the former and CS_2 and CO_2 the latter have been discussed. AX_3 has 4 frequencies and the equations are correlated with the typical cases of several trichlorides. The fourth frequency is usually a prominent one in the Raman spectra

and is attributed to an oscillation of the central atom along the symmetry axis against the plane of the X atoms. When A happens to be very light, certain alterations are produced in the general features of the scattered spectrum, typical example being that of BCl_3 which shows only two Raman frequencies. The constants used in the evaluation of the frequencies indicate that the altitude of the pyramid increases progressively as we pass from phosphorus the lightest to bismuth the heaviest. AX_4 has again 4 frequencies and the equations are discussed with reference to the Raman spectra of various tetrachlorides. The third frequency which arises out of an isotropic vibration of the central atom within the tetrahedron comes out in the scattering with prominence.

From a general survey of all the models it seems clear that such of the oscillations as involve relatively small or no change in the electric moment of the molecule often manifest themselves very prominently in the Raman spectra.

1. *Introduction.*

The mechanism of the new phenomenon of light scattering has been pictured by Sir C. V. Raman immediately after the discovery in a simple manner wherein the incident quantum of radiation is supposed to exchange energy with the molecules with which it encounters and reappears as a scattered quantum of altered energy. If E_k and E_l represent two energy levels of a molecule, the frequency ν_{kl} given by $E_k - E_l/_h$ manifests itself in the scattered spectrum in the form of various Raman lines represented by $\nu_o \pm \nu_{kl}$ where ν_o is the frequency of the incident quantum of radiation. Apart from a small proportion of excited molecules, under the average conditons of experiment a great majority of them are in the normal or vibrationless state, and the transitions are therefore constituted mostly by changes of the form $0 \longrightarrow 1$ in the vibrational quantum numbers. On this view most of the Raman transitions represent the fundamental vibration frequencies of the molecule involved in the scattering process. A correlation of the natural frequencies as revealed in the

Raman spectra with the molecular structure can therefore be effected through a study of the characteristic modes of oscillation of certain simple types of polyatomic models. From a purely dynamical point of view the subject has been first tackled by Dennison [1] who has investigated the systems of the type AX_2, AX_3 and AX_4 represented by special cases like CO_2, NH_3 and CH_4. The author has recently studied the Raman spectra of several simple molecules so chosen as may reasonably be represented by one or other of the molecular models X_2, X_3, X_4 or AX_2, AX_3 and AX_4. A brief consideration of each model will be given here. The general principles are the same as those originally adopted by Dennison.

2. *Theoretical considerations.*

A system of n particles will in general have $3n$ degrees of freedom and hence its configuration can be specified by $3n$ generalised co-ordinates, but if the system is subjected to the restriction that either rotation or translation as a whole is not permissible, then 6 of these $3n$ co-ordinates can be ignored, three associated with translation and three with rotation, and the rest, *viz.*, $(3n-6)$ can be chosen in a variety of ways. Under these conditions the potential and the kinetic energies of the system may be expressed as positive definite quadratic forms in the $3n-6$ co-ordinates and their time derivatives respectively.

It is known from the theory of vibrations that if the kinetic and the potential energies of a vibrating system are given in the form

$$T=\tfrac{m}{2}\,(a_{11}\dot{q}_1^{\,2}+a_{22}\dot{q}_2^{\,2}\ldots\ldots a_1\dot{q}_2\dot{q}_1\dot{q}_2\ldots\ldots);$$

$$V=\tfrac{1}{2}\,(b_{11}q_1^{\,2}+b_{22}q_2^{\,2}\ldots\ldots b_1b_2q_1q_2\ldots\ldots)$$

[1] Astrophys. Jour., Vol. 62, p. 84, 1925 and Phil. Mag., Vol. 1, p. 195 (1926).

it is always possible to find a linear transformation of the co-ordinates such that the energies, when expressed in terms of the new co-orinates, have the form

$$T=\tfrac{m}{2}(\dot{q}_1^2+q_2^2.....);\quad V=\tfrac{1}{2}(\mu_1 q_1^2+\mu_2 q_2^2.....)$$

μ_1, μ_2...being constants and the transformed co-ordinates q_1, q_2...being the normal or principal co-ordinates. The fundamental frequencies with which the system is capable of oscillating are given by $\frac{1}{2\pi}\sqrt{\mu_1}$...etc. The system may be treated as equivalent to a number of independent Planck oscillators whose characteristic frequencies are identical with the above normal modes of vibration. Following Dennison, the assumption that the fields of force are central about each nucleus will be made and we concern ourselves only with the oscillations about an equilibrium configuration, the displacements of the individual particles from their mean positions at any instant being infinitesimal; the assumed centro-symmetry of the electron configuration remaining practically undisturbed at the instant of each displacement. It will however have to be remembered that the actual state of affairs in a molecule is far more complicated and the above assumptions can only lead to an approximate theory.

3. *Polyatomic Molecules of Elements.*

X_2: It is clear that a diatomic oscillator has only one degree of vibrational freedom and hence has only one fundamental frequency of oscillation. Typical cases of hydrogen, nitrogen, oxygen and chlorine may be cited here as examples. The frequency shifts as revealed in their Raman spectra, *viz.*, 4162, 2331, 1555 and 556[1] respectively are in almost perfect agreement with the primary oscillation frequencies in the normal states as calculated from band spectra data (4162,

[1] The former three are due to Rasetti and the fourth, *viz.*, chlorine is taken from another paper by the author.

2331, 1554, 555). Such a result would suggest at once that the fundamental oscillation frequencies are involved in the production of a great many of the Raman lines. This view will now be further examined in more complex cases. In exceptional cases, however, a weak harmonic may be detected.

$\mathbf{X_3}$: For such a system 3 co-ordinates are necessary to represent the configuration at any moment and are chosen as the mutual displacements along the three sides of the triangle represented by q_1, q_2 and q_3. In accordance with the above assumptions, the energy functions may be written as

$$T=\frac{m}{2}\{P(q_1^2+q_2^2+q_3^2)+R(q_1q_2+q_2q_3+q_1q_3)\}$$

$$V=\frac{k}{2}(q_1^2+q_2^2+q_3^2).$$

The coefficients can easily be evaluated by letting each co-ordinate vary independently and studying the consequent motion of the nuclei under the conditions that there is no resultant angular or linear momentum consistent with the ignoration of the 6 co-ordinates associated with translation and rotation of the system. The kinetic energy takes the form

$$T=\frac{m}{2}\left\{\frac{5}{9}\left(\dot{q}_1^2+\dot{q}_2^2+\dot{q}_3^2\right)-\frac{2}{9}\left(\dot{q}_1\dot{q}_2+\dot{q}_2\dot{q}_3+\dot{q}_1\dot{q}_3\right)\right\}.$$

The characteristic determinant whose roots determine the normal modes of vibration may be written as

$$\left(m\lambda-3k\right)^2\left(m\lambda-\frac{3k}{2}\right)=0 \qquad \ldots \quad (1)$$

and is of the third order and is evidently degenerate in that it has only two distinct roots. The normal frequencies of this system are therefore given by

$$\frac{1}{2\pi}\sqrt{\frac{3k}{2m}};\ \frac{1}{2\pi}\sqrt{\frac{3k}{m}}$$

where k is a constant representing the binding force between any two atoms. The actual case in which the theory may be tested is that of ozone, the experimental difficulty in which case is considerable but the author however hopes to study it at a later date.

X_4 : The model of X_4 will next be considered. There are two probable arrangements of the nuclei in space namely, all the four being in the same plane and at the corners of a square, or in space at the corners of a tetrahedron. Six co-ordinates are necessary to specify the configuration and these will be chosen as the mutual displacements along the four sides and the two diagonals of the square in the former case and as the displacements along the edges themselves in the latter. The constants entering the kinetic energy functions can similarly be determined by allowing the co-ordinates to vary independently subject to the same restrictions as before and the functions written as

$$T=\frac{m}{2}\left\{\left(\dot{q}_1^2+\dot{q}_2^2+\dot{q}_3^2+\dot{q}_4^2\right)+\frac{1}{2}\left(\dot{q}_5^2+\dot{q}_6^2\right)+\left(\dot{q}_1\dot{q}_2+\dot{q}_1\dot{q}_4+\dot{q}_3\dot{q}_2+\dot{q}_3\dot{q}_4+\dot{q}_1\dot{q}_3+\dot{q}_2\dot{q}_4\right)-\frac{5}{4\sqrt{2}}\left(\dot{q}_1\dot{q}_6+\dot{q}_4\dot{q}_6+\dot{q}_2\dot{q}_6+\dot{q}_3\dot{q}_6+\dot{q}_1\dot{q}_5+\dot{q}_2\dot{q}_5+\dot{q}_3\dot{q}_5+\dot{q}_4\dot{q}_5\right)\right\}$$

and $$T=\frac{m}{2}\left\{\frac{5}{8}\left(\dot{q}_1^2+\dot{q}_2^2+\dot{q}_3^2+\dot{q}_4^2+\dot{q}_5^2+\dot{q}_6^2\right)-\frac{1}{4}\left(\dot{q}_1\dot{q}_2\cdots\cdots\dot{q}_5\dot{q}_6\right)+\frac{1}{4}\left(\dot{q}_1\dot{q}_6+\dot{q}_2\dot{q}_4+\dot{q}_3\dot{q}_5\right)\right\}$$

for the square and the tetrahedral models respectively. The characteristic determinant is of the sixth order in either case and may be written respectively as

$$\left(\lambda-\frac{2k_1}{m}\right)^3\left(\lambda-\frac{2k_2}{m}\right)\left\{5\left(\frac{m\lambda}{2}\right)+4\left(\frac{m\lambda}{2}\right)\left(k_1+5k_2\right)-4k_1k_2\right\}=0 \qquad \ldots \quad (2)$$

and $(m\lambda-2k)^3\ (m\lambda-4k)\ (m\lambda-k)^2=0$ ... (3)

for the two models, k_1 and k_2 in equation (2) are constants representing the force between the atoms along a side and a diagonal of the square respectively. k in equation (3) represents the force between the atoms along the edge of the tetrahedron. The system is evidently degenerate in either case in that it has 6 degrees of freedom and has only 4 independent modes of oscillation for the square model and 3 for the tetrahedral one.

An actual case of such a system may be sought for in the molecule of phosphorus, P_4, whose Raman spectrum has been studied by the author. The entire spectrum arises out of three independent frequencies in accordance with a tetrahedral model, the actual values being 374, 468 and 607. Such an inference is in agreement with the fact that yellow phosphorus belongs to the cubic system of crystals. It will be seen from equation (3) that the frequencies are given by

$$\nu_1=\frac{1}{2\pi}\sqrt{\frac{k}{m}};\ \nu_2=\frac{1}{2\pi}\sqrt{\frac{2k}{m}};\ \nu_3=\frac{1}{2\pi}\sqrt{\frac{4k}{m}}$$

their ratio being $1:\sqrt{2}:2$. In the actual case however, the frequencies do not strictly conform to such a ratio, a fact which may be explained if we remember that the conclusions are subject to certain limitations especially if the distribution of the fields of force is more complicated than that assumed.

It will be interesting to note that the third of the three Raman frequencies observed is the most intense one which, as will be seen later, is the general result observed with analogous tetrahedral models of the kind AX_3 and AX_4. In both cases there are always four Raman lines, the third in the AX_4 and the fourth in the AX_3 being generally the most prominent. In fact from the linear transformations performed, it may be deduced that this frequency represents the oscillation in which the whole tetrahedron is expanding symmetrically,

and it is significant that such an oscillation comes out with great intensity in the Raman spectrum.

We may now pass on to the more complicated systems with a central atom namely AX_2, AX_3 and AX_4. All the three cases have been worked out by Dennison and his equations will be adopted here. Several other investigators have tackled these systems by independent methods and arrived at practically the same conclusions.

4. *Triatomic Molecules.*

AX_2: The characteristic determinant for such a triatomic molecule may be written in the form

$$\left(\frac{m\lambda}{K_1}-1-\frac{2m}{M}\sin^2\alpha\right)\left\{\left(\frac{m\lambda}{K_1}\right)^2-2\left(\beta+\frac{1}{2}+\frac{m}{M}\cos^2\alpha\right)\frac{m\lambda}{K}+\frac{2\beta\cos^2\alpha}{\mu}\right\}=0 \qquad \ldots (4)$$

where

$$\beta=\frac{K}{K_1} \text{ and } \mu=\frac{M}{2m+M};$$

K_1 and K representing the binding between A and X and X and X respectively. M is the mass of A and m that of X. It will be seen that so long as α has a value other than 90° which is the case when the molecule is of a non-linear type, the system is non-degenerate and may be expected to give 3 independent vibrational frequencies. The equation was correlated by Dennison with the results obtained in the infra-red absorption of CO_2 on the assumption that it is a non-linear model, contrary to which however it is now well established that it is a linear molecule.[3] A molecule like SO_2, which is definitely known to be non-linear affords an interesting case. Its Raman spectrum is studied by the author from this point of view and the results are in excellent agreement with the theory in that it reveals three and only three independent oscillation

[3] F. I. G. Rawlins, Mol. Structure and Mol. Spectra, Rep. of Faraday Society, p. 995 (1929).

frequencies corresponding to infra-red wave lengths 19·0, 8·73 and 7·46μ which presumably represent the fundamental frequencies of the molecule. It may be noted here that the gas has been found by Coblentz to exhibit two prominent absorption bands in the infra-red at 8·64 and 7·41μ in agreement with the above.[4] The region of 19μ is beyond the range of his investigation. There are three arbitrary constants entering into the characteristic determinant and hence the evaluation of the three frequencies will afford no unique proof of the theory. On the other hand the factors that govern the intensity relationships in the infra-red spectra are entirely different from those that are responsible for the Raman spectra and hence the arguments used by Dennison in the case of CO_2 for testing the theory cannot be employed here.

The transformations performed in reducing the energy functions to their normal co-ordinates suggest, that of these three modes of oscillation, in the motion corresponding to the linear root of the characteristic determinant the sulphur atom vibrates in the plane of the triangle along a line perpendicular to the symmetry axis, the oxygen atoms remaining fixed, whereas in the motion corresponding to the other two roots, it vibrates along the line of symmetry, the oxygen atoms going apart or coming near each other symmetrically. An upper limit for the force between the sulphur and oxygen atoms may be deduced from a comparison of their dissociation energies in SO and SO_2. Making use of this limiting value for the constant K_1, a correlation of the observed frequencies with those contained in equation (4) is attempted and it is found that the linear root can be associated only with the lowest frequency namely 526, yielding a real value for α. The two larger frequencies 1146 and 1340 are obviously due to the sulphur atom vibrating along the symmetry axis, the more intense one corresponding to the more symmetric vibration.

[4] J. Lecomte, Spectre Infrarouge, p. 320 (1928).

By putting $\alpha=90°$ in equation (4) it can be so modified as to be applicable to certain special cases where the three constituent atoms are all in the same line. The equation takes a form in which it has only two finite roots given by

$$\frac{m\lambda}{K'} = 1 + \frac{2m}{M} \text{ or } 2\beta+1.$$

Two typical molecules which are conspicuous for their non-polar nature are CO_2 and CS_2 and are particularly suitable for a study of light scattering from the above point of view. The very fact that both these molecules give only two principal Raman frequencies—the one analogous to the third at 526 in SO_2 being absent in both of them—may be connected with the linearity of the former unlike the triangular model of SO_2. Contrary to the case of SO_2, in neither of these substances has any absorption been recorded in the infra-red corresponding to the Raman frequencies. Various attempts have been made to interpret these frequencies, especially in CO_2, as due to difference combinations of the observed infra-red absorption bands. In the interpretation of the infra-red spectrum of CO_2 prominent ones at 2·72 4·25 and 14·47μ have been taken as fundamental oscillations, but such a view is now clearly untenable in view of the accepted collinear model for CO_2 which implies an inactive fundamental [5] and hence not manifested in the infra-red absorption. The case of CS_2 is entirely analogous and offers similar difficulties.

The appearance of two principal frequencies in these cases is no doubt in agreement with the above theory, but in both cases they are so close that a more detailed examination is necessary. In the first instance it may be stated that Rasetti has succeeded in observing two more feeble lines in the vicinity

[5] Eucken, Z. Phys., Vol. 37, p. 714 (1926). See also Ghosh and Mahanti, Phys. Zeit., Vol. 30, p. 531 (1929).

of the above in CO_2, and Krishnamurti has similarly recorded weak lines in CS_2 in the neighbourhood of the principal frequencies. Appearance of these new frequencies, although very weak, is in direct disagreement with the above theory. A study of the polarisation in CS_2 leads one to believe that all these Raman lines represent in reality only one oscillation, the principal or the unperturbed frequency being represented by the most intense line of the group, all the others being in essence slight modifications of the same. The modification may be introduced either by a readjustment, however slight it may be, of the electron configurations in the molecule itself or by a possible departure from perfect linearity in a small proportion of the molecules.[6] This assumes that the essential characters, geometrical or otherwise, of all these subsidiary oscillations to be largely akin to those of the principal one. This is not surprising if we remember a similar case of the frequency usually associated with the C—H bond which is often multiple in various complex compounds and it is hard to say if the phenomena are really analogous. In fact the entire infra-red spectrum of CO_2 for instance cannot be successfully explained on the view that these two are distinct and the only fundamental oscillations. It is also significant that such close companions have only been detected[7] in CS_2 and CO_2 whereas the analogous case of N_2O according to Rasetti, Dickinson and Dillon gives only one Raman line, a fact which may probably be connected with the presence of the carbon atom in the former molecules.

Such an explanation leaves us facing the problem of finding out the second frequency which is predicted by the theoretical model and yet undetected in either CO_2 or CS_2. The only explanation is that it is far too weak and diffuse to be detected under ordinary conditions, a view which finds support if we compare the relative intensities of the lines in the

[6] See McCrea, Proc. Camb. Phil. Soc., Vol 23, p. 890 (1927).

[7] Phys. Rev., Vol. 34, p. 582 (1929).

analogous case of SO_2 where the principal line 1146 is many times more sharp and intense than the other two diffuse and weak lines.

5. *The Trichlorides.*

AX_3: The atoms in this model are assumed to be at the apices of a pyramid. The characteristic determinant is given by Dennison in the form of the equation

$$\left\{ l^2-2\left(\frac{3}{2}\mathrm{L}+\frac{1}{6}+\frac{c^2}{2\mu a^2}\right)l+\frac{3\mathrm{L}c^2}{\mu a^2}\right\}\left\{ l^2-2\left(\frac{3}{4}\mathrm{L}+\frac{1}{12}+\frac{b}{12\mu}\right)l+\frac{\mathrm{L}b}{4\mu}\right\}^2=0 \qquad (5)$$

where

$$l=\frac{m\left(c^2+\frac{a^2}{3}\right)\lambda}{k_1a^2}\ ;\ \mu=\frac{\mathrm{M}}{3m+\mathrm{M}}$$

$$\mathrm{L}=\frac{k}{k_1}\left(\frac{c^2+\frac{a^2}{3}}{a^2}\right) \text{ and } b=1+6\mu\frac{c^2}{a^2}$$

The system is again degenerate in that it has two double roots and hence only four independent modes of oscillation are possible although it has six degrees of freedom. c and a represent the height and the side of the basal triangle of the pyramid respectively. The other letters have the usual significance. Of these four frequencies, those corresponding to the linear roots, say ν_1 and ν_2, represent oscillations in which the central atom vibrates along the symmetry axis, while the **X** atoms move in or out symmetrically with respect to the axis of the pyramid. The double roots correspond to the oscillations in which the central atom vibrates normally to the symmetry axis.

Before discussing the validity of these conclusions the case of ammonia may be considered here in detail. It belongs to the type AX_3 under consideration and affords an interesting case in that its infra-red spectrum has been fully analysed by

various investigators. The band at 10·5 μ is associated with the oscillation in which the hydrogen atoms recede from the symmetry axis as the nitrogen is approaching their common plane. This band is found to have a peculiar structure in that it has two close and prominent Q branches which is intimately connected with the fact that the altitude of the pyramid is very small and the nitrogen atom has two equilibrium positions, corresponding to two close minima in the potential energy function, one on either side of the plane.

On the other hand, the band at 3μ is associated with a similar vibration in which the three hydrogens and the nitrogen move in or out at the same time. Of the other two fundamental modes in which the nitrogen may be expected to move in directions normal to the symmetry axis, one may be identified with the band at 6μ in the infra-red absorption. It must be noted now that all these three fundamental oscillations are revealed in the Raman spectra at 3303, 1580 and 1070, the former coming out with relatively much greater intensity, a fact which is of great significance, as it will be seen that intense Raman lines in all the trichlorides represent just such oscillations in which the central atom moves against the plane of the X atoms as they keep going in or out symmetrically.

Going back to the equation (5), it will be seen that there are three constants entering into the equation which depend on the dimensions of the molecular model and also on the nature of the distribution of the interatomic forces; a correlation of the observed frequencies in such models with the theory can only be effected by assuming reasonable values for the same. The table below sets forth the calculated and observed values together with the assumed molecular constants which result in the best fit.*

* When $BiCl_3$ is dissolved in strong HCl, the lines corresponding to the two lowest frequencies run together and form a band. The values given correspond to the edges of the unresolved band. Data for $SbCl_3$ are taken from Daure.

Substance		P^2	$k \times 10^{-4}$	$k_1 \times 10^{-4}$	ν_1	ν_2	ν_3	ν_4
PCl_3	Cal.	0·224	7	19	498	255	500	178
	Obs.				512	260	488	190
$AsCl_3$	Cal.	0·5	6	14	388	230	396	144
	Obs.				410	193	370	159
$SbCl_3$	Cal.	0·706	6	8·7	343	148	320	128
	Obs.				360	155	320	130
$BiCl_3$	Cal.	1·0	5	4·4	293	140	280	91
	Obs.				290	130	240	90

The table reveals many interesting features. The constant P which represents the ratio of the altitude of the pyramid to the side of the basal triangle increases as we go up the series P, As, Sb and Bi. Atoms like nitrogen, boron or aluminium which are lighter than phosphorus, the lightest in the series, may therefore be expected to form pyramids of low altitude approaching plane structures. The effect of such a relatively light central atom is manifested very clearly in the characteristic oscillations of certain molecules to be discussed a little later. The constant k_1 which represents the force between the central atom and the chlorine atom increases rapidly with decreasing atomic weight as may be expected. The variation is in qualitative agreement with the empirical rule suggested by Mecke from the band spectra data, *viz.*, $\nu\sqrt{z_1 z_2}$=constant, where ν is the frequency of oscillation of two bound atoms of atomic numbers z_1 and z_2. It must however be remembered that the rule is essentially intended for diatomic oscillators, whereas we are dealing here with oscillations of a much greater complexity.

Unlike this, the constant k which represents the force between the chlorine atoms themselves shows from compound

[1] Z phys., Vol. 42, p. 390 (1927).

to compound very little variation. This result may be interpreted as suggesting that their mutual distances remain practically unchanged, the variation in P being largely due to a variation in the altitude of the pyramid itself.

Mention may now be made of a special case of the AX_3 type wherein the A atom happens to be in the plane of the X atoms. As examples the cases of carbonates and nitrates may be cited. Several investigators have computed the frequencies of such a system on theoretical basis.[9] Special mention may be made of Nielsen who has followed up the methods originally adopted by Dennison. The four fundamental oscillation frequencies demanded by the theory for such a system come out in the Raman spectra of all nitrates and carbonates. Particular mention may here be made of the oscillation in which the three X atoms contract and expand symmetrically, hence producing no change in the electric moment of the molecule. Such an oscillation causes no direct absorption in the infra-red but it is just this that comes out with great intensity in the Raman spectra.

6. *Some Special Cases.*

NH_3, $CH Cl_3$, $CH Br_3$, $Al Cl_3$, $N Cl_3$, and $B Cl_3$[10]:— Special cases of AX_3 where A is relatively lighter are found in the above molecules. Such an exceptional character of the central atom is bound to produce alterations in the general characters of the Raman spectrum. It will first be noticed that whereas the fourth of the four frequencies always comes out with prominence in the Raman spectra of the trichlorides of P, As, Sb and Bi, NH_3 however gives only three, the third being the most intense. The fourth one is presumably very weak and hence not detected. As mentioned before the

[9] Amongst others see H. Kornfeld, Z. phys., Vol. 26, p. 205 (1924) and H. H. Nielsen, Phys. Rev., Vol. 32, p. 773 (1928).

[10] $CHCl_3$ and $CHBr_3$ can be classed under AX_3 if the (CH) group is treated as one unit.

analysis of the motion in each case reveals that the intense Raman line in all the cases including ammonia arises out of an essentially the same oscillation ; the one in which the central atom vibrates along the symmetry axis, the X's preserving symmetry about it.

Such an anomalous reversal of intensities in ammonia is presumably connected with the low atomic weight of the nitrogen atom. In addition to such a reversal, it will be noticed from the table that with the decreasing weight of the central atom in the trichlorides, the forces between the chlorines and the central atom are becoming relatively more prominent than those existing between the chlorines themselves, a state of affairs which in the limiting case would result in the disappearance of two of the frequencies as may be seen by putting $k=0$ in the equation (5). Such a case is actually met with in that of boron, the lightest of the trivalent elements. This trichloride reveals only two frequencies 255 and 471[11] the second one being more prominent, evidently corresponding to the intense Raman line (the fourth if the central atom is heavy enough or the third if it is light) in this series of compounds. Data are however not available for the cases of aluminium and nitrogen. Chloroform and bromoform show similar results in that besides the frequencies which may be attributed to hydrogen, they give a spectrum consisting of four principal frequencies which fall into two rather close groups, the third one being relatively more prominent than others. There is however a fifth frequency in both these cases whose presence is difficult to understand on the above theory, a case which is in many respects analogous to that of an additional frequency in CCl_4 at about 1500. If this result is in any way connected with the common anisotropic carbon atom is more than what can be said from the available evidence.

[11] Unpublished results of the work done by the author in collaboration with Mr. S. Venkateswaran.

Another interesting fact may here be noted, *viz.*, the violently explosive character of NCl_3 unlike the trichlorides of P, As, Sb and Bi. Data regarding the heats of formation of the various trichlorides are in agreement with the above anomalous behaviour of nitrogen chloride, in that its formation from nitrogen and chlorine is an endothermic reaction unlike that of all the other trichlorides which is exothermic. This is not surprising if we remember that the first member of a series in the periodic table often differs from its companions. Such an endothermic formation of the molecule and the explosive character must in some way be connected with the molecular model, which presumably differs from the usual tetrahedron.

7. *The Tetrachlorides.*

AX_4 : The system possesses nine degrees of freedom and is degenerate by virtue of its high degree of symmetry in that it has four normal frequencies given by—

$$\frac{1}{2\pi}\sqrt{\frac{k_2}{m}}\left(4\alpha+1\right)^{\frac{1}{2}} \; ; \; \frac{1}{2\pi}\sqrt{\frac{k_2}{m}}\left(\alpha-\frac{\beta}{4}\right)^{\frac{1}{2}}$$

$$\frac{1}{2\pi}\sqrt{\frac{k_2}{m}}\left[\alpha+\frac{5}{9}-\frac{13}{36}\beta+\sqrt{\left(\alpha+\frac{5}{9}-\frac{13}{16}\beta\right)^2-\left(\frac{8}{9}\alpha-\frac{16}{9}\alpha\beta-\frac{10}{9}\beta-\frac{4}{9}\beta^2\right)}\right]^{\frac{1}{2}}$$

$$\frac{1}{2\pi}\sqrt{\frac{k_2}{m}}\left[\alpha+\frac{5}{9}-\frac{13}{36}\beta-\sqrt{\left(\alpha+\frac{5}{9}-\frac{13}{16}\beta\right)^2-\left(\frac{8}{9}\alpha-\frac{16}{9}\alpha\beta-\frac{10}{9}\beta-\frac{4}{9}\beta^2\right)}\right]^{\frac{1}{2}}$$

where $\alpha=\frac{k_1}{k_2}$ and $\beta=\frac{k'}{k_2}$; k_1, k_2 and k' are constants.

These are arbitrary and enter in the potential energy function. In the motion associated with ν_1 the tetrahedron expands or contracts symmetrically, the central atom remaining fixed at the centre of gravity; in that coresponding to the double root ν_2 the X atoms move on the surface of a sphere. The Planck oscillators connected with ν_3 and ν_4 may be treated as isotropic in that they are triple roots of the determinant. This isotropic character is no doubt the result of a high degree

of symmetry imposed on the theoretical model, a departure from which may be expected in the actual molecules resulting in a splitting up of any one or all of the three degenerate frequencies ν_2, ν_3 and ν_4. Here again three constants enter the equations and hence an evaluation of the frequencies which are four in number may be achieved only by assuming suitable values for the same.

As typical instances, a detailed investigation of the light scattering in the tetrachlorides of carbon, silicon, titanium and tin is conducted and the results will be discussed here in the light of the above theory. It will be seen from the table given by the author in another paper that all these substances (with the exception of CCl_4) give four and only four Raman frequencies in entire agreement with the above theory which in itself is sufficiently convincing proof that these represent the fundamental oscillation frequencies in these molecules. Besides, the general characters such as the intensity and the polarisation relationships follow the same order in all these compounds. It will first be seen that the four Raman lines fall into two groups giving the spectrum an appearance of two rather close doublets in every case. Such a distribution of frequencies follows naturally from the model. To illustrate this, the case of CCl_4 will be considered in detail. The constant β is directly connected with the nature of the forces between the X atoms and it assumes a limiting value of zero if besides the Coulomb forces there are also electronic configurations perfectly symmetrical about each of the X atoms. It is interesting to note that the best fit with the observed values could be achieved only when β is made to take the limiting value zero. The constants k_1 and k_2 representing the forces between the carbon and the chlorine atoms themselves respectively are given the values 16×10^4 and 15×10^4. The calculated frequencies are given in the table below together with the observed ones.

CCl_4

Frequency	ν_1	ν_2	ν_3	ν_4
Calculated	290	770	154	459
Observed	310	770	216	459

As we proceed up the series, the same phenomenon as in the case of the trichlorides namely, a continual diminution of all the characteristic frequencies takes place which may be expected if they are really the fundamental oscillations in view of the fact that the vibrating system is being loaded with central atoms of increasing atomic weight. The doublet distribution of the frequencies is however preserved in every case. Of the above four frequencies ν_1 and ν_2 represent oscillations in which the chlorine atoms alone are taking part, the latter being a double root in the theoretical model. It will be seen that in the actual case of CCl_4 it has split up into two different frequencies of more or less equal intensity, a case of great significance which may be taken as an evidence for a slight departure of the molecular model from a perfect tetrahedron. The other tetrachlorides however show nothing of the kind and offer a unique support to the above theory in that the entire Raman spectrum in each case can be interpreted as arising from four and only four fundamental frequencies, combinations between themselves or overtones being absent in all cases. In the oscillations corresponding to ν_3 and ν_4 the carbon atom vibrates about its mean position, the probability of excitation being the same in all directions as each arises out of a triple root of the determinant. Special mention need be made here of one of these namely ν_4, which is particularly intense in all the four cases.

As further examples of this model, several cases may be suggested. Some of them namely, SO_4, ClO_4, MnO_4 etc., in the

ionic state will be briefly considered here. The structure of these ions is presumably tetrahedral with the oxygens situated at the corners of the tetrahedron. It is interesting to note that the Raman spectra of aqueous sulphates and perchlorates are very similar to each other and are in perfect agreement with the above considerations. In table below, data taken from Taylor are given [12]

SO_4	450	614	989	1218
ClO_4	453	614	937	1140

The dynamics of such a system is quite the same as for AX_4 model and by analogy it may be concluded that the third frequency, which is also prominent in the above cases, is due to the central atom vibrating about its mean position within the tetrahedron. The case of MnO_4 is exceedingly interesting as a prominent vibration frequency of 785 is observed by Taylor [13] and by independent arguments he concludes that this represents an oscillation of the manganese atom within the tetrahedron.

8. *Variation of the principal frequencies with environment.*

As may be expected the free oscillations of the above groups are only present in the ionic state and differ from those of the unionised molecules to an extent depending on the restrictions which the hydrogen in the acids or the metal atom in the salts is capable of imposing on the freedom of the group. Even the oscillations of the free ion are appreciably influenced by the distribution of the surrounding molecules in a solvent, the influence varying considerably with the nature of the solvent. [14] This alteration which is of a relatively small

[12] Rep., Faraday Society on Mol. Spectra and Mol. Structure, p. 830 (1929).
[13] *Ibid*.....p. 860 (1929). [14] See Taylor, loc. cit.

magnitude does not affect the foregoing discussion, as every ion (SO_4, ClO_4, CO_3, etc.) in combination continues to manifest its characteristic frequencies which still (except for the above noted small difference due to the combined atom) follow the same general relationship of intensity and magnitude.

A different kind of influence is seen in the interesting series of SO, SO_2, SO_3 and SO_4. As we go up the series, the obvious inference is that the increasing oxygen atoms result in an increasing complexity accompanied by a greater number of degrees of freedom. The table below illustrates the interesting points.

SO			1117*	
SO_2		526	1146	1340
SO_3		534	1068	1403
SO_4	450	614	989	1218

The frequencies given in the table, except for SO, are all obtained from a study of the Raman effect. Nisi [15] has however recently reported two additional lines in 10% H_2SO_4 corresponding to 893 and 1046 of which the latter is somewhat prominent. Such a result may be due to the fact that either the tetrahedron of the SO_4 ion has an intrinsic imperfection or is influenced very easily by the surroundings. This view is in accordance with the fact that there are striking variations in the frequencies of the ion with increasing dilution. The approximate agreement between the principal frequency 1146 of SO_2 and 1117 of SO is of significance if we remember that the calculated energy of dissociation of sulphur and oxygen from the band spectra data of SO is 148 kilo calories

* The frequency is taken from band spectra data. See V. Henri and F. Wolff, Jour. De. Phys., Vol. X, p. 81 (1927).

[15] Jap. Jour. Phys., Vol. 5, p. 119 (1929).

whereas the energy of dissociation as determined from the decomposition of SO_2 is 146·3 kilo calories.[16] Contrary to this however, as we pass on to SO_3 and SO_4 there is a definite diminution of this principal frequency.

9. *Relation between intensity and the character of oscillations.*

A comprehensive survey of the intense Raman lines in all the models discussed before in relation to the characters of the corresponding oscillations reveals interesting results. The principal lines in the cases of AX_2 and AX_3 are caused by the oscillations of A along the symmetry axes, the X's in either case preserving symmetry about them. The oscillation is therefore one in which there is a more or less symmetric expansion or contraction of the molecule as a whole. Similarly the intense line in the tetrahedral model of X_4 is attributed to a symmetric motion of the nuclei along the radial lines. All these cases involve relatively small or no change in the electric moment of the molecule as a whole and hence cause only weak absorption in the infra-red. Such of these oscillations are termed optically inactive and can only be detected indirectly when they combine with an active oscillation giving rise to absorption. Typical cases of such oscillations are presented by the principal Raman lines in the nitrates and carbonates. The result is not in any way surprising if we remember that the conditions which determine the intensity of a Raman transition are quite different from and much more complicated than those that are responsible for infra-red absorption. In fact, according to the wave-mechanical interpretation given by Hill and Kemble, a Raman transition corresponding to $E_k - E_l$ can always take place if there is a third energy level existing *simultaneously* with E_k

[16] V. Henri and F. Wolff, *loc. cit.*

and E_l with which both of them can combine even if the direct transition $E_k \longrightarrow E_l$ is forbidden by the usual selection rules. The intensity depends on the nature and the number of the third levels with which the initial and final ones in the Raman transition can combine. It is however not clear why the case of a symmetric oscillation is particularly favourable for the appearance of a prominent Raman line.

Unlike these cases, the principal line in the tetrachlorides and other molecules of the type AX_4 is attributed to a three-dimensional oscillation of the central atom within the tetrahedron. This oscillation involves an appreciable change in the electric moment of the molecule and causes direct absorption in the infra-red. In estimating the intensity of absorption for such frequencies, Dennison takes the *a priori* probability of such states to be 3 times that of a state represented by single roots of the characteristic determinant. Such oscillations may be expected to come out quite as prominently in the infra-red absorption unlike the previous cases of symmetric ones. As examples the cases of SO_4 and ClO_4 may be cited.[17] So far as the Raman spectra are concerned the oscillation can be interpreted as one which can be excited along all the three co-ordinate directions with equal probability, such a transition giving rise to a prominent and well-polarised Raman line.

In conclusion the author desires to express his best thanks to Prof. Sir C. V. Raman for his kind interest in the work.

[17] See Taylor, *loc. cit.*